



1352-2310(95)00059-3

STUDIES ON NO AND N<sub>2</sub>O FLUXES FROM A WHEAT FIELD

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(First received 20 June 1994 and in final form 18 January 1995)

**Abstract**—The importance of soil parameters and the other environmental conditions that affect emission rates of NO and N<sub>2</sub>O were studied over a fertilised wheat field. Open-chamber and closed-chamber techniques were used for the flux measurement of NO and N<sub>2</sub>O, respectively. Both gases showed variation in the emission rates which followed the seasonal variation in the available NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> and the moisture content of the soil. Whilst N<sub>2</sub>O emission rates increased with the moisture content of the soil, NO emissions decreased with increasing soil moisture and rainfall. The results suggested that most soil variables and atmospheric parameters had similar effects on both NO and N<sub>2</sub>O emission rates but that the overriding influence upon the NO/N<sub>2</sub>O emission ratio is the soil moisture content. The NO flux showed a clear diurnal variation which followed the surface soil temperature with an activation energy of 108 kJ mol<sup>-1</sup>. The annual NO flux estimated from this study (0.79 kg N ha<sup>-1</sup>) was approximately half the corresponding N<sub>2</sub>O (1.42 kg N ha<sup>-1</sup>).

**Key word index:** Nitric oxide, nitrous oxide, surface fluxes, wheat field.

## INTRODUCTION

Nitrogen gases, nitric oxide (NO) and nitrous oxide (N<sub>2</sub>O) are important species both in the atmosphere and in the cycling of nitrogen within the soil-atmosphere system. Nitrous oxide is the most naturally abundant oxide of nitrogen in the atmosphere (1300 Tg N) with a concentration of about 310 ppb that is increasing at around 0.3% yr<sup>-1</sup>. Nitric oxide (NO) and nitrogen dioxide (N<sub>2</sub>O) collectively referred to as NO<sub>x</sub> are the most abundant anthropogenic oxides of nitrogen in urban areas due to combustion of fossil fuels (Hao *et al.*, 1987). However, their concentration in clean air is less than 1 ppb (Carroll *et al.*, 1992).

Nitrous oxide is chemically a rather unreactive gas with an atmospheric lifetime of about 150 yr. In contrast, NO<sub>x</sub> is very reactive with a short lifetime of about 1.5 d and thus relatively large fluxes are required to maintain small atmospheric mixing ratios. On the other hand, even a small variation in the fluxes results in a large variation in the atmospheric mixing ratios (Conrad, 1990). N<sub>2</sub>O absorbs infrared radiation through several absorption bands in the wavelength region 7.7–17 μm (Ramanathan *et al.*, 1985), with

a net greenhouse effect per unit mass about 300 times greater than CO<sub>2</sub> (Rodhe, 1990). The contribution of N<sub>2</sub>O to global warming is about 5% over the last 100 years (Bouwman, 1990). Because N<sub>2</sub>O has a long lifetime and is unreactive it may reach the stratosphere by transport and diffusion, hence it is a natural *in situ* source of stratospheric NO due to its reaction with singlet oxygen (Cicerone, 1987). In fact, there is evidence that N<sub>2</sub>O does release far more NO into the stratosphere than any other source (Jackman *et al.*, 1980). This results in a reduction of the ozone layer and consequently increases the potential health hazards caused by more penetration of UV irradiation. NO acts as a catalyst in various reaction chains, thereby influencing the concentration and distribution of atmospheric O<sub>3</sub> and OH radical, the latter being the major reactant for a number of atmospheric constituents (Parrish *et al.*, 1990), believed to initiate most atmospheric oxidation processes (Shepherd *et al.*, 1991).

The principal sources of N<sub>2</sub>O are microbial nitrification and denitrification processes in soils and natural waters. Major sources of NO<sub>x</sub> include fossil fuel combustion, biomass burning and atmospheric lightning. However, there are major uncertainties concerning the budget of atmospheric NO and N<sub>2</sub>O and great uncertainties in the magnitude of the global biogenic source. About 44% of the Earth's land surface is

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covered with ecosystem types for which NO flux data, for example, are not available (Davidson, 1991). Fluxes of nitrogen gases into the atmosphere depend on a complex interaction between transport and biological production and consumption in the soil (Keller *et al.*, 1988). These in turn are mainly affected by soil conditions such as soil moisture, temperature, pH and nutrient levels as well as the agricultural practices within any field. Therefore, it is very important to evaluate the relative contribution of these processes to the total NO and N<sub>2</sub>O fluxes from the soil, and to measure fluxes of both gases simultaneously under natural field conditions to understand better mechanisms and factors controlling NO and N<sub>2</sub>O fluxes.

In this paper, factors affecting NO and N<sub>2</sub>O fluxes were studied intensively over a site through seasonal monitoring of the exchange pattern of these gases under different soil conditions and agricultural practices.

## EXPERIMENTAL

### Site

The flux measurements were made at Little Hoos field at the Institute of Arable Crop Research, Rothamsted Experimental Station, 50 km north of London, Grid reference TL 124 134. The soil (Batcombe series) was well drained, or moderately well-drained flinty loam on clay with flints and/or chalk, and about 115 m above sea level. The approximate composition of the soil was 52% sand, 26% silt and 22% clay (Talibudeen *et al.*, 1978). The field was a large (3.8 ha) uniform area planted with wheat. The pH of the field was about 7 throughout the whole experimental period. Fertiliser nitrogen as a mixture of ammonium nitrate and calcium carbonate (Nitram) was applied on 5 April 1991 and 22 April 1992 at a rate of 200 and 150 kg N ha<sup>-1</sup>, respectively.

### Flux measurements

NO and N<sub>2</sub>O flux measurements were carried out using soil chamber methods. Chambers used in this study were constricted from a galvanised metal box of dimensions 50 × 7.5 × 20 cm similar to that used by Ryden and Dawson (1982) and Goulding and Webster (1989). The small size of the chamber made it possible to insert it between the crop rows which were up to 1 m in height. NO fluxes were measured using the open-chamber technique as its analytical procedure requires a continuous flow of air. In this method clean air was passed into the chamber and the NO concentration in the effluent stream was used to calculate the flux. N<sub>2</sub>O was measured using the closed-chamber technique in which the flux is measured by periodically collecting gas samples from the chamber headspace and determining the change in N<sub>2</sub>O concentration with time. The differences in the emission rates measured by the above two techniques are generally insignificant within the achievable precision, limited by the spatial and temporal variability usually associated with the chamber techniques (Ambus *et al.*, 1993). During the measurements the chamber was closed by clamping a perspex lid with a foam rubber seal coated with a silicone sealant which fitted tightly on the chamber. For N<sub>2</sub>O measurements the lid had an air sampling port fitted with a septum to allow withdrawal of samples by means of plastic syringes (PLASTIPAK) fitted with a three-way stopcock valve (NIPRO). For NO flux measurements the lid had two air sampling ports and ambient air was pumped into the

chamber through an entry port at a rate of 2 ℓ min<sup>-1</sup> via a column of activated charcoal to remove NO<sub>x</sub> and O<sub>3</sub> from the air stream. This avoids the reaction NO<sub>x</sub> with O<sub>3</sub> leading to significant losses of NO. It is also important because it improves the precision of the measurement by removing the fluctuating ambient NO<sub>x</sub> levels (Shepherd *et al.*, 1991). A portion (1.55 ℓ min<sup>-1</sup>) of the effluent stream was analysed *in situ* for NO. When the concentration of NO at the outlet of the chamber was zero, the charcoal scrubber was removed in order to determine a downward flux, if any, to the soil. All connections and tubing from the chamber to the instruments were made from PTFE. All inside walls of the chambers were covered with a PTFE film TYGAFLOR to ensure a minimum uptake of the soil-emitted NO by the walls.

### Sampling and analysis

NO was analysed *in situ* either by a chemiluminescent NO–NO<sub>2</sub>–NO<sub>x</sub> analyser (Environement SA, model AC 30M) or by an LMA-3 NO<sub>2</sub> analyser (Scintrex Unisearch) preceded by a chromium trioxide (17%) NO to NO<sub>2</sub> converter. N<sub>2</sub>O samples were analysed by a Hewlett Packard 5790A gas chromatograph equipped with an <sup>63</sup>Ni electron capture detector held at 350°C. Samples were injected via a 1 ml loop gas sampling valve into a packed PTFE column (1.5 m × 4 mm i.d.) of Porapak N (80–100 mesh) held at 60°C. The GC was attached to an integrator (Shimadzu C-R3A) and the mixing ratio was determined from the peak height and compared against standards of N<sub>2</sub>O in nitrogen. Further details of the experimental set-up and the precision of the analysis are given by Yamulki (1993).

Soil temperature within the chamber was measured by a digital thermocouple inserted 2 cm into the soil. In addition to the flux measurements a number of soil parameters were also measured from the area (top 10 cm) surrounding the chamber. Soil samples were kept frozen for later analysis. Soil pH was measured in a 1:2.5 soil:water suspension. Soil moisture content (% of dry weight) was determined gravimetrically, and soil available NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (mg N ℓ<sup>-1</sup> soil solution) were determined by extracting 62 g soil with 200 ml 2 M KCl and subsequent colorimetric analysis (APHA, 1976).

## RESULTS AND DISCUSSION

### Seasonal variability

Results of a total of 68 N<sub>2</sub>O flux measurements and 62 NO flux measurements are plotted as daily averages against the day of the measurement between March 1991 to May 1992 (Figs 1 and 2, respectively). The data points represent an average of 1–9 flux measurements on each day during the 15 months of observation. The corresponding results for the soil mineral nitrogen [(NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup>) – N] concentrations, soil temperature and soil moisture content are given in Fig. 3. The results show a substantial variation in N<sub>2</sub>O emission rates throughout the measurement period with values ranging from –3 ng N m<sup>-2</sup> s<sup>-1</sup> (absorption by the soil) to 46 ng N m<sup>-2</sup> s<sup>-1</sup> (emission from the soil). NO however showed a more constant emission throughout the early part of the study period with flux values ranging from 0.16 to 4 ng N m<sup>-2</sup> s<sup>-1</sup>; only after day 450 did the emission increase markedly to 42 ng N m<sup>-2</sup> s<sup>-1</sup>. Generally, emission rates seemed to follow the mineral nitrogen content, with maximum NO and N<sub>2</sub>O fluxes occur-

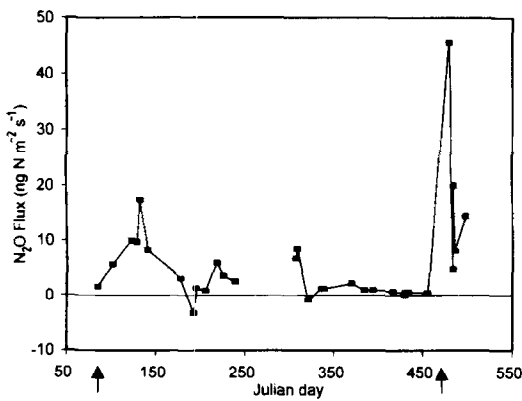


Fig. 1. Seasonal cycle of N<sub>2</sub>O emission flux measured using the closed-chamber method, 1991–1992. Arrows indicate time of fertiliser application.

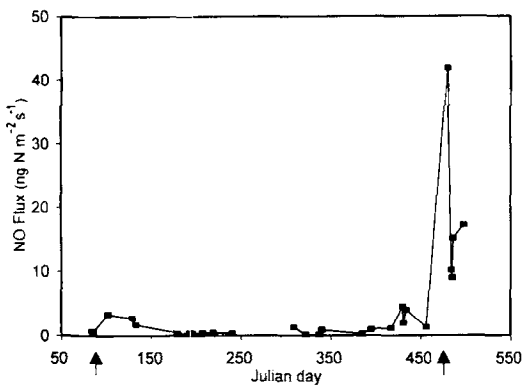


Fig. 2. Seasonal cycle of NO emission flux measured using the open-chamber method, 1990–1992. Arrows indicate time of fertiliser application.

ring after fertiliser application on days 95 and 478. Emission rates peaked on day 480, two days after the application of fertiliser in the second year and decreased sharply thereafter. Similarly, the lowest emission rates were observed during the period from day 179 to 456 when the soil available  $\text{NH}_4^+$  and  $\text{NO}_3^-$  dropped to its background level of about  $2 \text{ mg N } \ell^{-1}$ . The peak flux of N<sub>2</sub>O after the first fertiliser application in 1991 was not observed, which may have been due to the fact that the first N<sub>2</sub>O flux measurements were carried out one week after the application of fertiliser.

The dependence of N<sub>2</sub>O emission rates on soil available  $\text{NH}_4^+ + \text{NO}_3^-$  ( $r^2 = 0.74$  and  $n = 17$ ) during the study period are shown in Fig. 4a. The corresponding dependence of NO emission rates on  $\text{NH}_4^+ + \text{NO}_3^-$  ( $r^2 = 0.78$  and  $n = 16$ ) is shown in Fig. 4b. The effect of soil mineral nitrogen seems to override the other soil variables such as soil temperature and soil moisture content. During summer and autumn when the soil mineral N was low there was

a period of fluctuation in the N<sub>2</sub>O emission rates with values ranging from  $-3.3$  to  $8.6 \text{ ng N m}^{-2} \text{ s}^{-1}$  which followed the soil moisture content. The negative value on day 193 indicates an absorption of N<sub>2</sub>O by the soil microorganisms which was probably due to the period of a high temperature and low soil moisture content (total cumulative rainfall for 10 d prior to day 193 was 1.9 mm). Bowden *et al.* (1991) observed a similar uptake of N<sub>2</sub>O by the soil during the summer and early autumn.

Fertiliser was applied as  $\text{NH}_4\text{NO}_3$ ; therefore, it was not possible to distinguish between the effect of the individual components of the fertiliser (i.e.  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) on NO and N<sub>2</sub>O emission rates and thus whether NO and N<sub>2</sub>O emissions were due to nitrification or denitrification processes in the soil. However, indirect relationships to other soil parameters, such as soil moisture content that affect the nitrification–denitrification status may give an indication of the processes involved. In this study both N<sub>2</sub>O and NO were correlated with the soil moisture content (Figs 5a and b, respectively). A positive correlation was observed between N<sub>2</sub>O and the soil moisture content ( $r^2 = 0.41$  and  $n = 21$ ), while NO was found to be inversely correlated to the soil moisture content ( $r^2 = 0.47$  and  $n = 15$ ). Similar results have also been observed between soil moisture content and N<sub>2</sub>O (Conrad *et al.*, 1983; Skiba *et al.*, 1992; Drury *et al.*, 1992) and between soil moisture content and NO (Shepherd *et al.*, 1991; Drury *et al.*, 1992; Slemr and Seiler, 1991) or between NO and rainfall (Johansson and Granat, 1984; Skiba *et al.*, 1992). In water, oxygen diffuses four orders of magnitude slower than in the gas phase (Drury *et al.*, 1992). High soil moisture content therefore reduces the diffusivity of oxygen into the soil, increasing the anaerobic microsites and consequently the rate of denitrification, which favours emissions of N<sub>2</sub>O. Whilst the results suggest that N<sub>2</sub>O might have been produced by denitrification, the inverse correlation between NO and the soil moisture content indicates that NO production was mainly due to nitrification. NO diffuses some  $10^5$  times slower through water than through an equivalent thickness of air (Galbally, 1989). Thus, increasing soil moisture content will increase the residence time of denitrification gases and hence facilitate the subsequent conversion of NO to N<sub>2</sub>O and N<sub>2</sub>. The recent work of Cardenas *et al.* (1993) indicates a peak in NO emissions from savannah soil at a moisture content of ca. 12%, with reduction at lower and higher moisture levels. Our data fall within the range of 17–28% soil moisture and show behaviour consistent with that seen by Cardenas *et al.* at higher levels of soil moisture.

#### Diurnal variability

The effect of soil temperature on emission rates of NO and N<sub>2</sub>O was not clear. This may be due to the overriding effect of the soil mineral N and the moisture content. In order to study the effect of soil

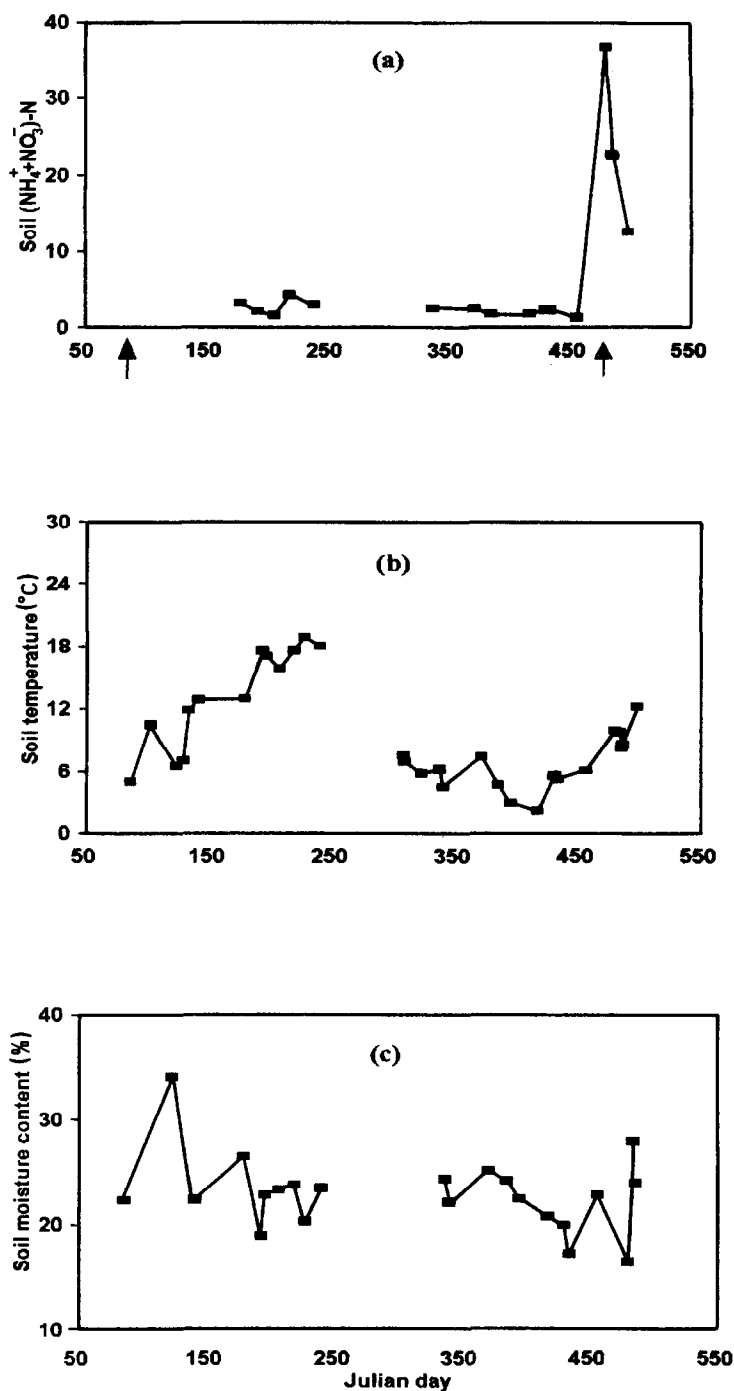


Fig. 3. Seasonal cycle of (a) soil  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  ( $\text{mg N } \ell^{-1}$ ), (b) soil temperature (2 cm depth) and (c) soil moisture content (% of dry weight), 1991–1992. Arrows indicate time of fertiliser application.

temperature on both NO and  $\text{N}_2\text{O}$  emission rates, a small-scale diurnal study was carried out during the 29th and 30th of April 1992, seven days after the application of fertiliser. Measurements of both gases were made simultaneously from two chambers approximately 2 m apart. The soil moisture content was 23.8% and the exchangeable  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  was 12.9 and 11.6  $\text{mg N } \ell^{-1}$ , respectively. The soil

temperature was measured at 2 cm depth; diurnal temperature changes were modest with temperature variation over a range of only  $5^{\circ}\text{C}$ .

The data show a clear diurnal variability of NO emission with changes in soil temperature (Fig. 6). Variation in the NO emission rates were quite large with values ranging from 7 to 17  $\text{ng N m}^{-2} \text{s}^{-1}$ . A strong correlation between NO emission rates and

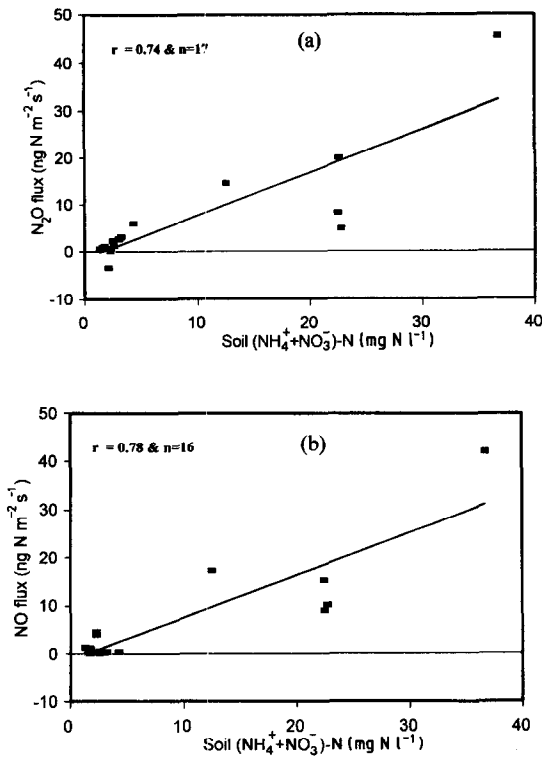


Fig. 4. Dependence of emission flux of (a) N<sub>2</sub>O and (b) NO on the soil nitrogen concentration.

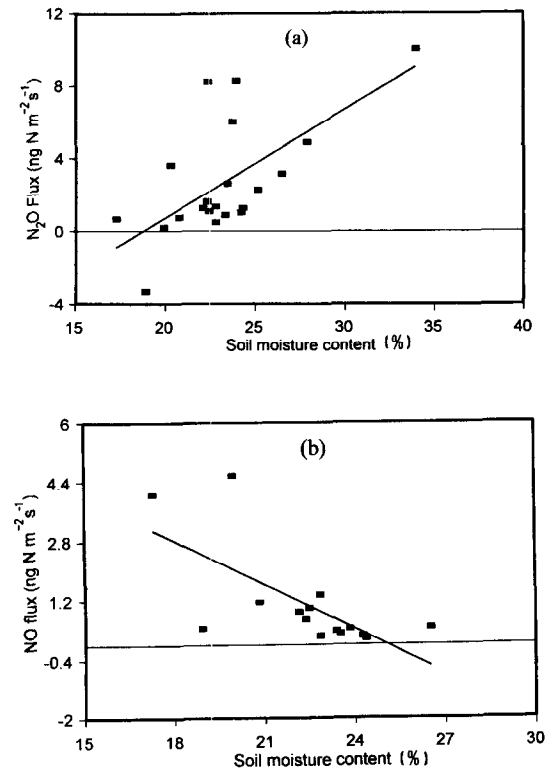


Fig. 5. Dependence of emission flux of (a) N<sub>2</sub>O and (b) NO on the soil moisture content (% of dry weight).

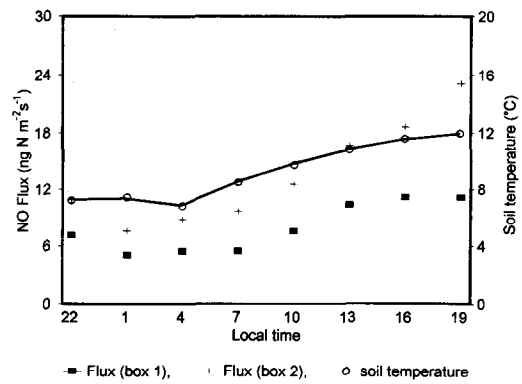


Fig. 6. Diurnal variations of the NO flux, and the soil temperature (2 cm depth) 29–30 April 1992.

soil temperature ( $r^2 = 0.88$  and  $n = 8$ ) and air temperature ( $r^2 = 0.93$  and  $n = 8$ ) was observed. The activation energy for the NO emission rate was  $108 \text{ kJ mol}^{-1}$ , calculated from the Arrhenius equation

$$\ln \text{NO emission} = \ln A - E_a/RT_s$$

where  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T_s$  is the soil temperature (K),  $A$ , the pre-exponential factor is a constant, and  $E_a$  is the activation energy which was calculated from the slope of the line in Fig. 7. The activation energy calculated for NO emission in this study is larger than that found by Johansson and Granat (1984) ( $E_a = 65\text{--}83 \text{ kJ mol}^{-1}$ ), and it is at the upper level of those found by Slemr and Seiler (1984) ( $E_a = 44\text{--}103 \text{ kJ mol}^{-1}$ ); and Williams *et al.* (1988) ( $E_a = 97 \pm 11 \text{ kJ mol}^{-1}$ ). However, Shepherd *et al.* (1991) found a similar value of activation energy,  $108 \pm 20 \text{ kJ mol}^{-1}$ .

As the diurnal amplitude of temperature decreases with soil depth, Conrad and Seiler (1985) pointed out that the apparent activation energy N<sub>2</sub>O production will be higher than normal if N<sub>2</sub>O production processes occur at depths closer to the surface than the point of temperature measurement and lower than normal when the production processes occur at deeper depths. This reasoning also applies to NO production, and could explain the higher apparent activation energy calculated in this study than some other work.

Figure 8 shows the emission rates of N<sub>2</sub>O from the two chambers plotted against the local time. A clear diurnal variability in the rate of N<sub>2</sub>O emission was observed, with a maximum rate during the evening (8 p.m.) and the minimum emission rate in the morning (8 a.m.). The data suggest that the diurnal changes in the rate of N<sub>2</sub>O emission observed are not in phase with the diurnal changes in the temperature of the surface soil (Fig. 8). Diurnal variation in N<sub>2</sub>O production rates from soils has been attributed to temperature fluctuations in the soil (Denmead *et al.*, 1979; Conrad *et al.*, 1983). This is because the rate of biological reaction rises exponentially with temperature in

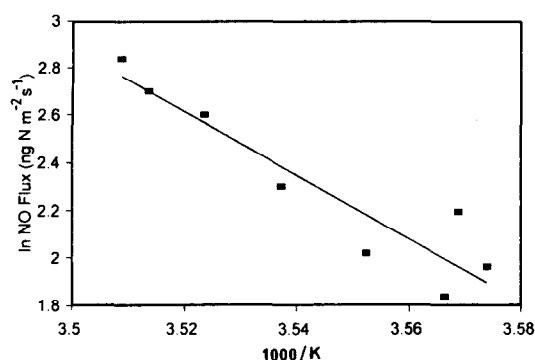


Fig. 7. Temperature dependence of the NO emission flux, 29–30 April 1992. Flux data are mean emission rates of the two chambers.

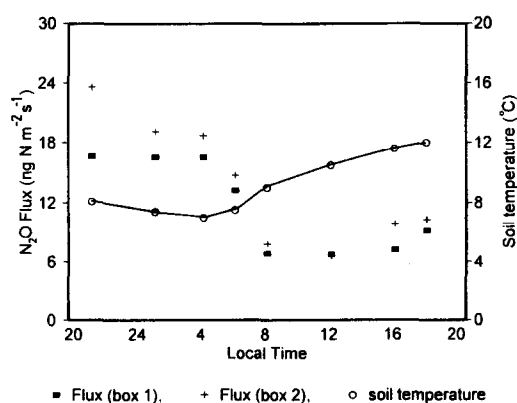


Fig. 8. Diurnal variations of the N<sub>2</sub>O flux and the soil temperature (2 cm depth), 29–30 April 1992.

the range 15–35°C (Warneck, 1988) and that soil temperature may increase the rate of diffusion of N<sub>2</sub>O from the soil profile. However, if N<sub>2</sub>O was produced via denitrification, a consistent exponential relationship between denitrification and soil temperature would be difficult to demonstrate (Aulakh *et al.*, 1992), since increasing temperature affects the solubility of O<sub>2</sub> and thus its consumption. The time lag between the maximum and minimum rate of N<sub>2</sub>O emission and the maximum and the minimum soil temperature observed in this study indicates that most of the N<sub>2</sub>O emitted was produced in the subsoil layer, probably by denitrification, since the temperature maxima and minima occur progressively later with increasing soil depth (Conrad *et al.*, 1983).

The results of the diurnal pattern observed in this study are in good agreement with those found by Blackmer *et al.* (1982). However, they propose that the diurnal N<sub>2</sub>O emission pattern should be attributed to diurnal changes in the solubility of N<sub>2</sub>O in soil water caused by the changing soil temperature profile. Many authors however have found a clear positive correlation between N<sub>2</sub>O emission rates and soil tem-

perature and quote activation energies ranging from 20 to 166 kJ mol<sup>-1</sup> for microbial nitrification and denitrification (McKenney *et al.*, 1980; Conrad *et al.*, 1983). On the other hand, others have found little or no relationship between N<sub>2</sub>O emission rates and soil temperature (Bowden *et al.*, 1990; Skiba *et al.*, 1992) or between denitrification processes and temperature (Focht and Verstraete, 1977; Aulakh *et al.*, 1984).

#### Spatial variability

One of the most important characteristics of NO and N<sub>2</sub>O fluxes from terrestrial ecosystems is their high degree of spatial variability (Schimel *et al.*, 1988). This is usually due to localisation in the population of microorganisms responsible for NO and N<sub>2</sub>O production or consumption, and the parameters affecting their activities. It has been reported that in order to estimate the true mean flux of N<sub>2</sub>O within  $\pm 10\%$  of the estimated mean, approximately 350 flux measurements will be required on a 3 m by 36 m experimental plot (Folorunso and Rolston, 1984). Although this is impossible in practice, it is important to account for the spatial variability usually encountered with the chamber technique in order to quantify better and/or to extrapolate emission rates to larger areas. In this study the spatial variability within the field was studied on selected days before and after the application of fertiliser. Emission rates were measured from different areas on a plot approximately 2 m apart. Table 1 summarises the results of the spatial variability of N<sub>2</sub>O and NO, respectively, measured during the study. Despite the low N<sub>2</sub>O emission rates observed during the measurements a high degree of spatial variability was observed with a coefficient of variation (CV) ranging from 13 to 57%. Similar spatial variation was also observed for NO with coefficients of variation ranging from 17 to 47%. The spatial variability of both NO and N<sub>2</sub>O emission rates measured after the application of fertiliser did not show any increased variation. Previous studies have shown that the spatial variability may be approximately log normally distributed, in view of this, estimates of the spatial variability in Table 1 where the number of measurements is only 3 should be treated with caution.

On several occasions the short-term temporal variations in fluxes of both gases were also determined from consecutive half-hour average measurement of the fluxes from the same area. Table 2 shows that little variation in the emission rates of both N<sub>2</sub>O and NO was observed with coefficient of variation ranging from 6 to 14% for N<sub>2</sub>O and from 0 to 10% for NO. Johansson and Granat (1984) studied the temporal and spatial variability in NO emission rates and found similar results with a coefficient of variation ranging from 9–16% to 18–89%, respectively. However, they found that fertiliser application increased the spatial variability which was interpreted by the uneven distribution of the fertiliser pellets. Many authors have found a high spatial variability in the

Table 1. Spatial variability of N<sub>2</sub>O and NO emission rates (ng N m<sup>-2</sup> s<sup>-1</sup>)

| (a)                                  |       |                        |                              |     |
|--------------------------------------|-------|------------------------|------------------------------|-----|
| Date                                 | Time  | Number of measurements | Mean N <sub>2</sub> O fluxes | CV% |
| <i>Before fertilizer application</i> |       |                        |                              |     |
| 06-01-92                             | 02.30 | 3                      | 2.28                         | 45  |
| 20-01-92                             | 11.10 | 5                      | 1.03                         | 41  |
| 21-02-92                             | 12.30 | 3                      | 0.75                         | 24  |
| 05-03-92                             | 12.00 | 5                      | 0.24                         | 13  |
| 06-03-92                             | 11.40 | 5                      | 0.58                         | 57  |
| 09-03-92                             | 11.30 | 9                      | 0.68                         | 43  |
| <i>After fertilizer application</i>  |       |                        |                              |     |
| 24-04-92                             | 12.30 | 8                      | 45.60                        | 36  |

| (b)                                  |       |                        |                |     |
|--------------------------------------|-------|------------------------|----------------|-----|
| Date                                 | Time  | Number of measurements | Mean NO fluxes | CV% |
| <i>Before fertilizer application</i> |       |                        |                |     |
| 20-01-92                             | 12.10 | 3                      | 0.23           | 22  |
| 21-02-92                             | 11.50 | 3                      | 1.14           | 47  |
| 05-03-92                             | 10.50 | 5                      | 4.58           | 39  |
| 06-03-92                             | 11.00 | 5                      | 1.92           | 33  |
| 09-03-92                             | 11.00 | 8                      | 4.05           | 17  |
| <i>After fertilizer application</i>  |       |                        |                |     |
| 24-04-92                             | 10.30 | 8                      | 41.94          | 35  |

Note: Measurements were taken at different places within the plot (approximately 2 m apart).

Table 2. Temporal variability of N<sub>2</sub>O and NO emissions (ng N m<sup>-2</sup> s<sup>-1</sup>)

| (a)      |       |                        |                              |     |
|----------|-------|------------------------|------------------------------|-----|
| Date     | Time  | Number of measurements | Mean N <sub>2</sub> O fluxes | CV% |
| 07-08-91 | 11.30 | 2                      | 6.00                         | 9   |
| 28-08-91 | 11.45 | 3                      | 2.62                         | 14  |
| 06-12-91 | 11.20 | 3                      | 1.27                         | 6   |
| (b)      |       |                        |                              |     |
| Date     | Time  | Number of measurements | Mean NO fluxes               | CV% |
| 12-07-91 | 01.00 | 2                      | 0.45                         | 0   |
| 15-07-91 | 02.00 | 3                      | 0.25                         | 9   |
| 28-08-91 | 11.00 | 3                      | 0.30                         | 0   |
| 06-12-91 | 12.40 | 3                      | 0.87                         | 10  |

Note: Measurements were taken consecutively (at half hourly intervals) from exactly the same area.

N<sub>2</sub>O emission rates (Table 3). The spatial variability observed in this study are at the lower end of those shown in Table 3. This might be due to the more homogeneous soil conditions and distribution of both nutrients and microbiological activities than in those studies which observed higher variability.

Table 3. N<sub>2</sub>O spatial variability reported in the literature as a coefficient of variation of N<sub>2</sub>O emission rates.

| Author                            | CV%     | Area used          |
|-----------------------------------|---------|--------------------|
| Robbins <i>et al.</i> (1979)      | 31–168  | 400 m <sup>2</sup> |
| Mosier <i>et al.</i> (1981, 1982) | > 60    | —                  |
| Bremner and Blackmer (1980)       | 50      | 100 m <sup>2</sup> |
| Matthias <i>et al.</i> (1980)     | 31–168  | 100 m <sup>2</sup> |
| Folorunso and Rolston (1984)      | 282–379 | 1–2 m apart        |
| This study                        | 24–57   | 1–2 m apart        |

#### Annual NO and N<sub>2</sub>O fluxes and comparison between the results

Table 4 shows an estimate of the average fluxes of N<sub>2</sub>O and NO for each season and the total annual flux. The annual N<sub>2</sub>O flux was calculated at 1.4 kg N ha<sup>-1</sup> yr<sup>-1</sup> which was equivalent to less than 1% of the fertiliser applied and in good agreement with Ryden's (1981) estimate. The annual NO flux was about half (0.79 kg N ha<sup>-1</sup>) of this. Approximately, 55 and 82% of the annual N<sub>2</sub>O and NO fluxes, respectively, were emitted during the spring shortly after the application of N fertiliser.

The percentage loss of N<sub>2</sub>O during the spring was almost equal in spring 1991 and 1992. However in contrast, NO emissions during spring 1992 were higher by a factor of 7 than during spring 1991. During spring 1991 the total cumulative rainfall for a one-month period after the application of fertiliser was about 75 mm. The corresponding amount of rainfall during spring 1992 was only about 40 mm. The higher percentage loss of NO during spring 1992 compared to that from spring 1991 could therefore be due to the contrasting effect of the soil moisture content on the NO and N<sub>2</sub>O emissions which were observed during this study. As previously mentioned soil moisture content was positively correlated with N<sub>2</sub>O emission rates and negatively correlated with NO emissions. This is also consistent with the negative, albeit poor correlation observed between the NO/N<sub>2</sub>O emission ratio and soil moisture content ( $r = 0.54$  and  $n = 17$ ). The NO/N<sub>2</sub>O emission ratio was generally in favour of NO (greater than unity) during low soil moisture content and generally in favour of N<sub>2</sub>O (less than unity) during periods of high soil moisture contents. Laboratory studies have shown that the molar ratio of NO/N<sub>2</sub>O was found to be  $> 1$  in nitrified cultures, whereas for denitrifiers it has been found to be  $< 1$  (Anderson and Levine, 1986). This may be the result of the influence of O<sub>2</sub> on denitrification (Drury *et al.*, 1992). However, direct extrapolation to the field situation may be difficult, as nitrification and denitrification are likely to occur simultaneously (Skiba *et al.*, 1992).

Generally, a good correlation between fluxes of NO and N<sub>2</sub>O was observed throughout the entire study period ( $r^2 = 0.75$  and  $n = 26$ ). This suggests that the majority of soil and climatic factors had similar effects on both NO and N<sub>2</sub>O emission rates, the exception

Table 4. Average seasonal N<sub>2</sub>O and NO flux measured during March 1991–May 1992

| Season              | Mean N <sub>2</sub> O flux<br>(kg N ha <sup>-1</sup> ) | % loss <sup>a</sup> | Number of<br>observation |
|---------------------|--|---------------------|--------------------------|
| Spring <sup>b</sup> | 0.78   | 55                  | 39                       |
| Summer              | 0.16   | 11                  | 10                       |
| Autumn              | (0.38) <sup>c</sup>                                    | (27) <sup>c</sup>   | 3                        |
| Winter              | 0.10   | 7                   | 16                       |
| Total               | 1.42 <sup>d</sup>                                      | 100                 | 68                       |

(b)

| Season              | Mean NO flux<br>(kg N ha <sup>-1</sup> ) | % loss <sup>a</sup> | Number of<br>observation |
|---------------------|--|---------------------|--------------------------|
| Spring <sup>b</sup> | 0.65                                     | 82                  | 37                       |
| Summer              | 0.03                                     | 4                   | 11                       |
| Autumn              | (0.06) <sup>c</sup>                      | (8) <sup>c</sup>    | 2                        |
| Winter              | 0.05                                     | 6                   | 12                       |
| Total               | 0.79 <sup>d</sup>                        | 100                 | 62                       |

<sup>a</sup> Amount of the gas-N emitted during each season as a percentage of the total amount.

<sup>b</sup> Mean flux during spring 1991 and 1992.

<sup>c</sup> These data should be treated with caution because of the small number of observations.

<sup>d</sup> Annual flux.

being soil moisture which affects emission of the two gases in opposite senses.

### CONCLUSION

The current study showed a substantial variation in fluxes of NO and N<sub>2</sub>O which followed the seasonal variation of the soil moisture content and the soil mineral nitrogen nutrient level. The maximum flux of both gases was observed two days after an application of N fertiliser. Nitric oxide was solely emitted from the soil with flux values ranging from 0.16 to 42 ng N m<sup>-2</sup> s<sup>-1</sup>. Nitrous oxide showed both absorption and emission by the soil with values ranging from -3 to 46 ng N m<sup>-2</sup> s<sup>-1</sup>, respectively. Both the soil and the atmospheric conditions generally had similar effects on emission rates of NO and N<sub>2</sub>O. However, N<sub>2</sub>O fluxes increased with increasing soil moisture content and NO fluxes decreased with increasing the moisture content of the soil. This was reflected in an NO/N<sub>2</sub>O emission ratio which was generally in favour of NO during dry conditions and in favour of N<sub>2</sub>O during wet conditions. The diurnal pattern of NO fluxes showed a high dependence on the soil temperature with an activation energy of 108 kJ mol<sup>-1</sup>. A high spatial variability in emission rates of both NO and N<sub>2</sub>O was observed with coefficients of variation up to 47 and 57%, respectively. The annual NO and N<sub>2</sub>O flux from this field amounted to approximately 0.79 and 1.42 kg N ha<sup>-1</sup>, respectively. Extrapolating these fluxes to all U.K. arable land (4.4 × 10<sup>6</sup> ha) gives a total flux of 3.5 kt N and 6.3 kt N emitted as NO and N<sub>2</sub>O, respectively, each year.

It was estimated, that 0.93% of the fertiliser N was emitted as N<sub>2</sub>O and 0.53% as NO. The fertiliser-induced N<sub>2</sub>O emission was in good agreement with Eichner's estimate of 0.5–2% (Eichner, 1990). We estimated that the annual N<sub>2</sub>O and NO emissions from fertilised land in U.K. would be 0.014 and 0.008 Tg N, respectively, with a total annual N fertiliser consumption of 1.5 Tg. The estimate for N<sub>2</sub>O was lower than the figure used in the U.K. source inventory (0.022–0.036 Tg N yr<sup>-1</sup>) (INDITE, 1994). Fertilised land only accounted for 1.1% of the total U.K. NO<sub>x</sub> emissions (DOE, 1992).

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